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(54) Forming Uniform Multiconstituent Coatings on Glass

(57) In a method of forming a uniform coating 5 *of at least two constituents* on a hot vitreous support 4, at least one coating constituent precursor is sprayed *separately* from the other precursor(s), the separately sprayed precursors being sprayed over substantially co-extensive areas of the support 4 to form the uniform coating 5 and at least one of them being sprayed in aqueous solution.

The formed coating may comprise (a) tin oxide doped with fluoride, iron oxide or antimony oxide; or (b) indium oxide doped with tin oxide. Specified coating precursors are $SnCl_2$, tin dibutyl diacetate, $NH_4F \cdot HF$, $FeCl_3$, $SbCl_3$, indium chloride. Specified solvents are water, methanol, aqueous methanol, and DMF.

FIG.1

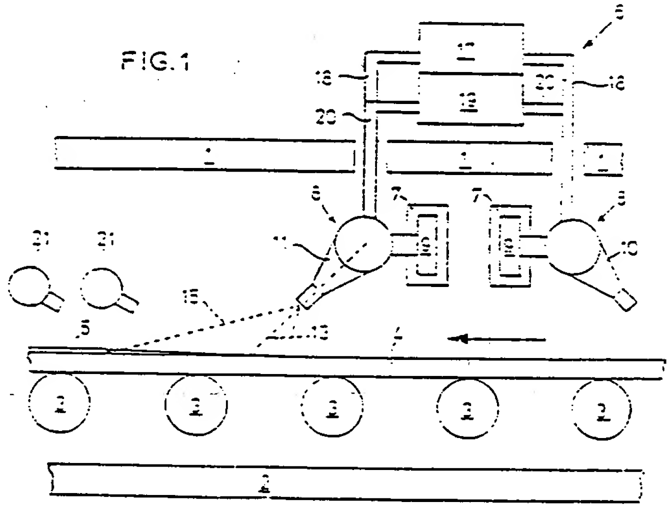

FIG.2

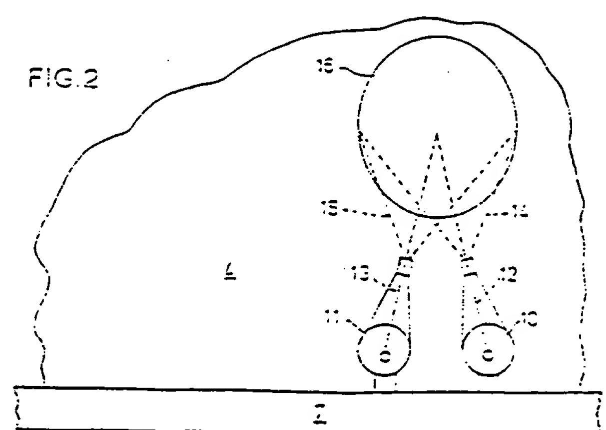

FIG.1

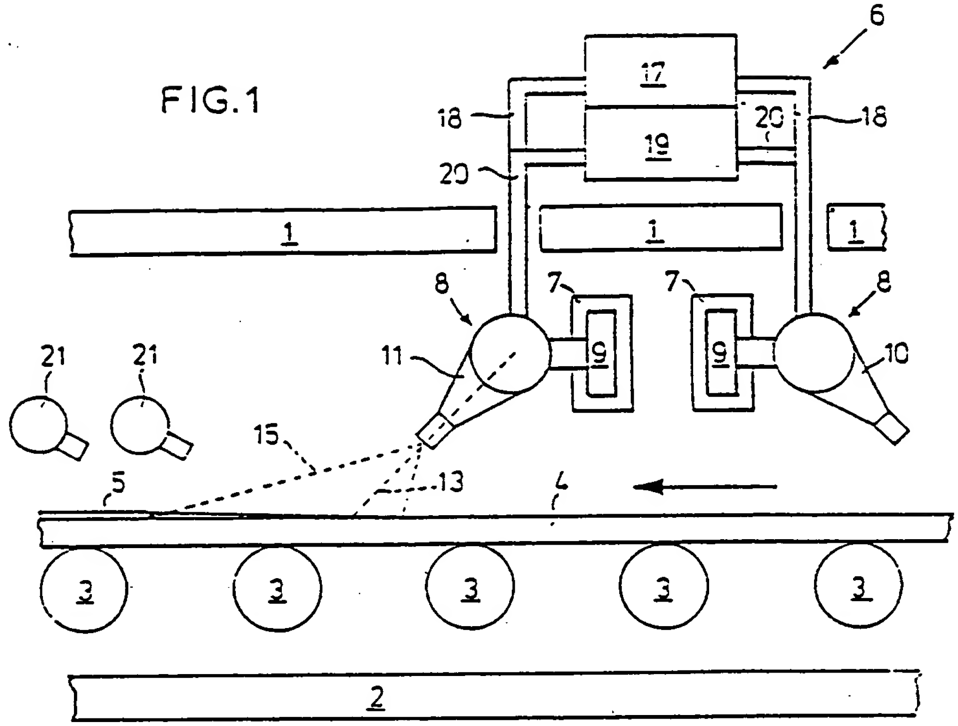
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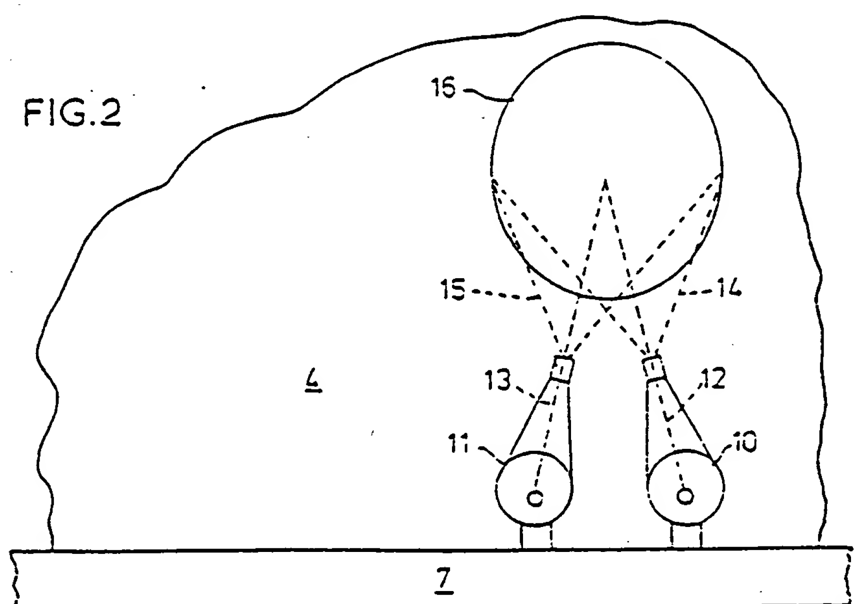
FIG.2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SPECIFICATION

Method and Apparatus for Coating Glass

This invenpon relates to a method of forming a uniform coating comprising at least two coating constituent substances on a vitreous support by spraying the support while in heated condition with coating precursor substances to form said coating by pyrolysis. The invention includes apparatus suitable for performing such a method.

Processes of the above kind are used for example to provide electrically conductive coatings which modify the effect of the support on incident electromagnetic radiation of various wavelengths. Such coatings are used inter alia to reduce the emissivity of the support in respect of infra-red radiation, especially such radiation having a wavelength greater than 5000 nm. When used for such purposes, such coatings are typically doped with an additive to increase the conductivity of the coating so that the coating will have an enhanced modifying effect on for example the infra-red reflectivity of the coated support. Processes of the above kind may also be used to form coatings which modify othe properties of the support, for example its apparent colour.

When using known processes, the rate at which a coating of a given thickness can be built up is inconveniently restricted. The coating rate can be increased within certain limits by increasing the concentration of the solution of coating precursor substances, but in many cases, the coating solution becomes unstable at high concentrations and this has undesirable effects. In particular, certain solutions of coating precursor substances tend to form gels at high concentrations and so cannot readily be sprayed. The coating rate can also be increased within certain limits by increasing the sprayed quantity of a coating solution of a given concentration. But this entails the spraying of greater quantities of solvent which must evaporate when it impinges against the heated vitreous support thus robbing the support of heat so that the necessary pyrolysis of the coating precursor substances is inhibited. Furthermore, above a certain spraying rate, it is impossible to form good quality uniform coatings because the spray droplets are too large and/or because the droplets have too high an impact force on the support.

Attempts have been made to form good quality coatings at higher build-up rates by spraying quantities of the coating solution simultaneously from two spray-guns, but the results have not been satisfactory in view of the large amount of solvent sprayed and the consequent large heat loss by the substrate.

It is an object of the present invention to provide a coating process which is applicable for forming multi-constituent coatings at a higher build-up rate than is possible by the known processes, and/or to allow greater latitude in the selection of coating precursor substances.

According to the present invention there is provided a method of forming a uniform coating comprising at least two coating constituent substances on a vitreous support by spraying the support while in heated condition with coating precursor substances to form said coating by pyrolysis, characterised in that at least one coating precursor substance is sprayed separately from the or at least one other such precursor substance, in that such separately sprayed precursor substances are sprayed over substantially coextensive areas of the support to form a uniform coating thereon and in that at least one of them is sprayed in aqueous solution.

The present invention accordingly substantially avoids risk of premature reaction between the separately sprayed coating constituent precursor substances, and this has the indirect effect that those substances may be sprayed in greater concentrations than has hitherto been possible and thus the coating can be formed at a higher build-up rate. The invention also allows greater latitude in the selection of coating precursor substances. For example by making use of the present invention it is possible to use precursor substances which, if mixed in a common solution, would react together, for example to throw down a precipitate, and even precursor substances for which there is no single solvent in which they are all sufficiently soluble for practical purposes.

In most preferred embodiments of the invention, said coating precursor substances are selected so as to give rise to a coating on the vitreous support which reduces the emissivity of the coated area in respect of infra-red radiation. This gives a product which is commercially highly desirable for use in glazing windows, of buildings for example. Preferably, at least one said coating precursor substance is selected and sprayed so as to give rise to a minor additive coating constituent and such precursor substance or precursor substances is or are sprayed in aqueous solution. In fact many of the additive precursors in view are soluble in water. Water is the least expensive and most universally available of all solvents.

In some preferred embodiments of the invention, a said coating precursor substance is selected and sprayed so as to give rise to a main coating constituent and such precursor substance is sprayed in a solvent which comprises water. It is however preferable not to use too large an amount of water especially when spraying the main coating constituent precursor substance in view of its latent heat of evaporation and the consequent loss of heat from the vitreous support as the sprayed solvent is vaporised on contact with the support. Accordingly, in the most preferred embodiments of the invention a said coating precursor substance is selected and sprayed so as to give rise to a main coating constituent and such precursor substance is sprayed in a solution which comprises an organic solvent. The organic solvent may be used alone or in some cases, in admixture with water. The organic solvent may be chosen for various properties apart from its capacity to dissolve the

or a main coating constituent precursor substance. For example, the organic solvent may be chosen from those which have a lower surface tension than water. This facilitates the formation of smaller droplets in the spraying process and this promotes a more uniform coating on the support. The organic solvent may be chosen from those which have a lower specific latent heat of evaporation than water in relation to their capacity to dissolve the main coating precursor substance. In this way, evaporation of the solvent on striking the support will remove less heat energy from the support. Indeed, the organic solvent may be chosen from those which react exothermically at or below the temperature of the heated support so that heat energy is in fact released. Methanol satisfies all three of these desiderata in respect of the coating precursor substances particularly in view and is an especially preferred solvent for use in the present invention.

The present invention is particularly suitable for use in situations where one said coating constituent is a metal oxide and another is a doping agent selected to increase the electrical conductivity of the metal oxide coating. For example, the present invention makes it possible to form a tin oxide (SnO_2) coating doped with fluorine ions from tin dibutyl diacetate as main coating constituent precursor and ammonium bifluoride ($NH_4F.HF$) as additive precursor. Tin dibutyl diacetate is substantially soluble only in organic solvents, while ammonium bifluoride is not substantially soluble in organic solvents.

While a dibutyl diacetate, or indeed other organic metal salts may be used as said metal oxide coating precursor substances, for reasons of cost and availability, it is preferred that said metal oxide coating precursor substance is an inorganic metal salt, amongst which, tin chloride and indium chloride are especially suitable for use in the formation of coatings respectively of tin oxide and indium oxide.

When operating in accordance with the invention, any coating precursor substance can be chosen solely with regard to the properties of the coating constituent to which it will give rise. In embodiments of the invention in which said metal oxide coating constituent precursor substance is tin chloride, it is advantageous to select a doping agent precursor substance from ammonium bifluoride and antimony chloride. In embodiments of the invention where said metal oxide coating constituent precursor substance is indium chloride, it is advantageous to use tin chloride as said doping agent precursor substance.

As an example of the benefits which are attainable when using the present invention, the specific case of forming fluorine doped tin oxide coatings starting from tin chloride and ammonium bifluoride may be cited. According to a currently used manufacturing process an aqueous solution containing 375 g/l of $SnCl_2.2H_2O$ and 55 g/l of $NH_4F.HF$ is sprayed at 20 litres per hour onto a glass ribbon 3 m wide advancing through the coating station at 1 m/minute to give a coating 750 nm thick. If it is desired to apply a similar coating to a faster moving ribbon where glass is being produced at a higher rate, it would be necessary to increase the amount of solution applied to the glass thus robbing the glass of heat, or to increase the strength of the solution with the consequent risk of gel formation. By spraying the $SnCl_2$ and the $NH_4F.HF$ separately in accordance with the invention, it is possible to increase the concentration of the $SnCl_2$ solution to as much as 1800 g/l in aqueous solution without giving rise to spraying difficulties. $NH_4F.HF$ is very soluble in water and may be sprayed in any desired concentration. Thus it will be seen that without increasing the volume sprayed, it is possible to form a similar coating as in the currently used process referred to above, without increasing the spraying rate and for a greater width and/or speed of glass ribbon advance past the coating station.

The invention is accordingly particularly useful where said support is a ribbon of glass which is sprayed over substantially its full width as it travels along an annealing lehr. The coating station can be located at a position in the lehr where the newly formed ribbon is at a suitable temperature, so that little or no supplementary heat has to be supplied, and for a given ribbon width and speed of advance, it is possible to form coatings of much greater thickness than has hitherto been possible.

The invention extends to a vitreous support bearing a uniform coating formed by the method, and includes apparatus for forming a uniform coating comprising at least two coating constituent substances on a vitreous support while in heated condition by spraying the support with coating precursor substances to form said coating by pyrolysis, characterised in that such coating apparatus comprises means for conveying the support in a predetermined horizontal direction (hereinafter called "forwardly") and at least one coating head comprising at least two spray guns, means for displacing the spray guns in tandem transversely across the path of the support, said spray guns being connected to at least two different coating solution reservoirs whereby the spray guns at at least one coating head are enabled to simultaneously spray different solutions onto the substrate to mix on or above the substrate during each transversal thereof, said spray guns being inclined to the horizontal so that the main horizontal component of the spray droplets is forward or rearward.

This apparatus is of simple construction and is well adapted to perform the spray-coating method of the invention.

When sprayed droplets are ejected from the spray guns, they will each form a cone and this cone will intersect the path to form a number of spray ellipses. These ellipses may be separate or they may be tangent to one another or they may be partly or wholly superimposed. This latter feature is preferred to give a high quality uniform

coating, and it is accordingly preferred that said spray guns are arranged with their axes convergent in the spraying direction.

Preferably said spraying means is located within an annealing lehr for spraying a ribbon of glass as it advances through the lehr from a ribbon forming machine. It is relatively simple to arrange the spraying means in the lehr at a position where the temperature of the glass ribbon is at suitable value to promote the required pyrolysis, and little or no supplementary heating means needs to be used, thus saving energy.

The present invention may be used to coat glass formed in any convenient way, for example by using a ribbon forming machine in which glass is drawn vertically from a bath of molten glass and then passed over a horizontal bending roll for conveyance along a horizontal annealing lehr, but is is preferred that said ribbon forming machine comprises a float tank.

Preferably, said spray guns arranged so that their discharge orifices are between 15 cm and 40 cm above the ribbon path.

Advantageously, the discharge orifices of at least one said coating head are at most 10 cm apart.

Preferably, said spray guns of at least one coating head are arranged so that the axes of their spray cones are convergent towards the ribbon path.

A preferred embodiment of apparatus in accordance with the invention will now be described in greater detail with reference to the accompanying diagrammatic drawings in which

Figure 1 is a diagrammatic cross sectional drawing of apparatus at a coating station within an annealing lehr, and

Figure 2 is a plan view of part of that appatatus.

In the drawings, an annealing lehr has a roof 1 and bottom wall 2. Spaced above the bottom wall 2 of the lehr are a plurality of conveyor rollers 3 for conveying a hot glass ribbon 4 through the lehr in the direction of the arrow. It is desired to provide the glass ribbon with a multi constituent coating 5 by pyrolysis in situ on the ribbon 4 as the ribbon passes beneath a coating station 6. The coating station 6 comprises an endless track 7 about which coating heads 8 carried by slides 9 are caused to move. Each coating head 8 comprises two spray guns 10, 11 which are aimed downwardly towards the ribbon path in such a way that the main horizontal component of droplets sprayed by them away from the spray head lies parallel to the direction of advance of the glass ribbon. Furthermore, it will be noted from Figure 2 that the axes 12, 13 respectively of the spray guns 10, 11 are convergent, so that the ellipses of contact of the spray cones 14, 15 emitted by those respective spray guns on the moving glass ribbon 4 are substantially coincident at 16. In variants of the embodiment illustrated, the spray guns 10, 11 are so directed that their spray-ribbon contact ellipses merely overlap, or are distinct.

Each spray gun 10 is fed with a first coating solution held in a reservoir 17 via a pipe 18, and each spray gun 11 is fed with a second coating solution from a second reservoir 19 via a pipe 20.

The coating heads 8 are arranged to circulate continuously around the endless track 7, and valve means (not shown) may be incorporated in the apparatus so that spraying takes place while the coating heads move along only one reach of the track 7 as they traverse the ribbon 4.

Optional exhaust ducts such as 21 may be provided forwardly of the zone of impingement of the spray cones 14, 15 to suck off excess spray droplets and decomposition products.

The following are examples of processes according to the invention performed with the aid of apparatus as above described.

Example 1

Coating apparatus as described was used for coating a ribbon of glass 3 metres in width after its production by a Libbey-Owens type drawing process while the still hot ribbon was travelling along an annealing lehr at about 4.5 metres/minute. The coating apparatus was installed at a position in the annealing lehr where the temperature of the glass at the zone of impingement of the spray droplet cone was about 600°C.

The spray guns were of a conventional type and were operated at a pressure of about 6 kg/cm^2. The coating heads were displaced around the track at a speed and relative spacing so as to give forty spraying passes per minute. The spray guns were located so that their orifices were 35 cm above the glass ribbon as they travelled across it, and their spray axes were at 30° to the horizontal, i.e. the plane of the glass ribbon. The two spray orifices on each coating head were located 8 cm apart, and the two spray guns were so directed that their spray cones both impinged on substantially the same area of the ribbon.

Suction forces in the exhaust ducts 21 were adjusted to maintain a depression of about 100 mm H_2O at their inlets which were located between 1 and 20 cm above the ribbon.

The first reservoir 17 was charged with an aqueous solution of tin chloride obtained by dissolving per litre of hot water, 1,600 grammes of anhydrous tin chloride ($SnCl_2$). The second reservoir 19 was charged with a solution containing 300 grams of ammonium bifluoride ($NH_4F.hf$) per litre of water.

The two coating solutions were fed to the respective spray guns of the coating heads on the spraying reach of the track and were discharged each at a rate of 18 litres per hour in an amount of 15 normal cubic metres of carrier gas per hour. A coating of tin oxide doped by fluorine ions and having a thickness of 750 nm was formed on the glass ribbon.

Examination of the coating showed it to be of uniform thickness and optical properties and to have a homogeneous structure. The coating had a neutral tint viewed by reflected light. The coating

possessed a high visible light transmissivity and possessed an appreciable reflective power in respect of infra-red radiation in the wavelength range 2.6 to 40 μm. The emissivity of the coating was 0.1.

Similar results were obtained in a process in which the same coating procedure was followed for coating a ribbon of float glass.

In a previously known process a similar coating of similar thickness was formed by spraying a single coating solution containing 375 grams $SnCl_2.2H_2O$ and 55 grams $NH_4F.HF$ per litre a total rate of 20 litres per hour and in 10 Nm^3/hr carrier gas from a single spray gun making eighteen spraying passes across a ribbon of the same width per minute. In order to achieve a coating of the same thickness as that afforded by the process described in Example 1 it was necessary for the glass ribbon to travel at about 1 metre per minute. The coating solution could not be sprayed at a sufficiently increased rate to allow a similar coating to be applied to a ribbon travelling at 4.5 metres per minute nor could the concentration of the single coating solution be sufficiently increased without unwanted reaction between the tin chloride and ammonium bifluoride taking place.

Example 2

A ribbon of float glass about 2.5 metres wide was coated with fluorine doped tin oxide to a thickness of 750 nm it travelled at about 4.5 metres per minute along an annealing lehr from the float tank.

The two coating solutions sprayed were respectively formed by adding tin dibutyl diacetate to an organic solvent namely methanol in an amount of 1180 grams per litre of solution and by adding ammonium bifluoride to water in an amount of 300 grams per litre.

The coating heads were arranged to make forty spraying passes across the ribbon per minute and they were mounted so that the spraying orifices were 6 cm apart and 35 cm above the ribbon. The axes of the spray guns at each head were parallel and inclined at 30° to the horizontal.

The organic tin solution (the main coating solution) was sprayed at a rate of 37 litres per hour using 20 Nm^3/hour of carrier gas, and the $NH_4F.HF$ solution (the doping solution) was sprayed at a rate of 15 litres per hour using 8 Nm^3/hour of carrier gas. The two solutions were fed to the spray guns so that for each coating head, the zone of contact of the main coating solution on the glass ribbon was the same as that of the doping solution.

It is not possible to form a coating using these coating precursor substances in a single solution, since there is no solvent which will dissolve them both in useful quantities.

In a variant of this Example, a main coating solution of 1180 grams dibutyl diacetate per litre of solution in dimethyl formamide was sprayed at a rate of 37 litres per hour. Other conditions were the same and the resulting fluorine doped tin oxide coating had a thickness of 750 nm.

Both coatings has uniform thickness and optical properties, were of homogeneous structure and of neutral tint in reflection. The emissivities of the two coatings were respectively 0.15 and 0.16 (approximately).

Example 3

Using a process similar to that of Example 1, a glass ribbon 3 m wide travelling at 4.5 metres/minute was sprayed with a main coating solution containing 1600 grams of $SnCl_2$ per litre of a solvent made up of equal volume proportions of water and methanol, and a colouring solution containing 90 grams $FeCl_3.6H_2O$ per litre of water as solvent to give a coating of tin oxide coloured with iron oxide. The main coating solution was sprayed at a rate of 2 litres per hour and the colouring solution was sprayed at a rate of 1.5 litres per hour to give a coloured coating 100 nm in thickness having uniform optical and physical properties. In fact this coating was yellowish-red in colour. The colour of such a coating can be varied simply by modifying the iron chloride solution, and without changing the conditions under which the tin chloride is sprayed.

Example 4

A tin oxide-antimony oxide containing coating was formed on a glass ribbon 2.8 metres wide travelling at 4.5 metres/minute by a process similar to that given in Example 1.

A first coating solution containing 1600 grams $SnCl_2$ per litre of water as sole solvent was sprayed at a rate of 18 litres per hour. A second coating solution was simultaneously sprayed and contained 150 grams of $SbCl_3$ per litre of water. The second solution was sprayed at a rate of 18 litres per hour. The resulting coating was 750 nm in thickness and when viewed in transmitted light it has a very intense blue tint.

By varying the amount of $SbCl_3$ sprayed onto the glass, and this is very much easier when it is in a separate solution from the $SnCl_2$, it is possible to vary the inensity of the colour and the electrical resistance of the coating. Such variation can be achieved by spraying the antimony solution at a greater or lower rate or by increasing or reudcing its concentration.

Claims

1. A method of forming a uniform coating comprising at least two coating constituent substances on a vitreous support by spraying the support while in heated condition with coating precursor substances to form said coating by pyrolysis, characterised in that at least one coating precursor substance is sprayed separately from the or at least one other such precursor substance, in that such separately sprayed precursor substances are sprayed over substantially coextensive areas of the support (4) to form a uniform coating (5), and in that at least one of them is sprayed in aqueous solution.

2. A method according to Claim 1,

characterised in that said coating precursor substances are selected so as to give rise to a coating on the vitreous support which reduces the emissivity of the coated area in respect of infra-red radiation.

3. A method according to Claim 1 or 2, characterised in that at least one said coating precursor substance is selected and sprayed so as to give rise to a minr additive coating constituent and in that such precursor substance or precursor substances is or are sprayed in aqueous solution.

4. A method according to Claim 3, characterised in that a said coating precursor substance is selected and sprayed so as to give rise to a main coating constituent and in that such precursor substance is sprayed in a solution which comprises an organic solvent.

5. A method according to any preceding claim, characterised in that a said coating precursor substance is selected and sprayed so as to give rise to a main coating constituent and in that such precursor substance is sprayed in a solvent which comprises water.

6. A method according to any preceding claim, characterised in that one said coating constituent is a metal oxide and another is a doping agent selected to increase the electrical conductivity of the metal oxide coating.

7. A method according to Claim 6, characterised in that said metal oxide coating precursor substance is selected from tin chloride and indium chloride.

8. A method according to any preceding claim, characterised in that said support is a ribbon (4) of glass and in that such ribbon is sprayed over substantially its full width as it travels along an annealing lehr (1, 2).

9. Apparatus for forming a uniform coating comprising at least two coating constituent substances on a vitreous support while in heated condition by spraying the support with coating precursor substances to form said coating by pyrolysis, characterised in that such coating apparatus comprises means (3) for conveying the support (4) in a predetermined horizontal direction (hereinafter called "forwardly") and at least one coating head (8) comprising at least two spray guns (10, 11) means (7, 9) for displacing the spray guns in tandem transversely across the path of the support (4), said spray guns (10, 11) being connected to at least two different coating solution reservoirs (17, 19) whereby the spray guns (10, 11) at at least one coating head (8) are enabled to simultaneously spray different solutions onto the support (4) to mix on or above the support (4) during each traversal thereof, said spray guns (10, 11) being inclined to the horizontal so that the main horizontal component of the spray droplets is forward or rearward.

10. Apparatus according to Claim 9, characterised in that said spray guns (10, 11) are sprayed with their axes (12, 13) convergent in the spraying direction.

11. Apparatus according to Claims 8 or 9, characterised in that said spraying means is located within an annnealing lehr (1, 2) for spraying a ribbon of glass as it advances through the lehr from a ribbon forming machine.

12. Apparatus according to any of Claims 9 to 11, characterised in that said spray guns (10, 11) are arranged so that their discharge orifices are between 15 cm and 40 cm above the path of the support (4).

13. Apparatus according to any of Claims 9 to 12, characterised in that the discharge orifices of at least one said coating head (8) are at most 10 cm apart.

14. Apparatus for coating a vitreous support substantially as herein described.

14. A method of coating a vitreous support substantially as herein described optionally using apparatus according to any of Claims 9 to 14.

16. A vitreous support which has been coated by a method according to any of Claims 1 to 8 and 15.

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